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(54) Biocide

(57) A method for the treatment of an aqueous system is described with comprises adding to the water an ethoxylated phenol and, optionally as biocides one of, heterocyclic compounds, quaternary ammonium compound, phenol or chlorinated phenols, amine or amide, halogen release agents, organic cyanides or thiocyanates, sulphones, tin compounds, aliphatic aldehydes, triazines, alkyl phosphonium compounds, bis bromo acetoxy butene or dithiocarbamates.

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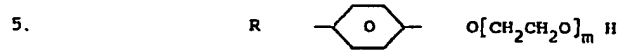
SPECIFICATION

Biocide

This invention relates to the treatment of aqueous systems, especially cooling water systems and water systems used in paper pulping and manufacture.

In industrial cooling water systems, for instance in industrial cooling towers, the water used is not, of course, sterile with the result that bacteria accumulate in the system and this quite commonly gives rise to a slimy deposit on the surfaces of the system which come into direct contact with the cooling water. A similar situation applies in paper making; slime can deposit on any of the surfaces with which the water comes into contact including the paper pulping bath, on the paper web and in the recirculating back pipework. A large variety of different microbiological control agents have been used for the purpose of killing these bacteria and/or inhibiting slime formation or for dispersing and killing microbiological slime. These chemicals are principally biostats such as lime or sulphur dioxide or, more generally, biocides, for example isothiazolones, methylene bis(thiocyanate), quaternary ammonium compounds and chlorine release agents.

Such biocides are, however, relatively expensive materials. It has now surprisingly been found, according to the present invention, that more effective biological control can be obtained if a variety of different biocides are used in combination with certain ethoxylated phenols. In effect, therefore, it has been found that it is possible to use less biocide by using the biocide in combination with certain ethoxylated phenols. According to the present invention there is provided a method for the treatment of an aqueous system which comprises adding to the water either an ethoxylated phenol having the general formula:

5. 

where m represents 2 to 40 and R represents $C_n H_{2n+1}$ in which n is from 0 to 18 without a microbiological control agent or a said ethoxylated phenol and a microbiological control agent which is a biocide as defined below.

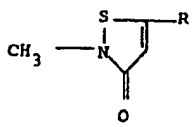
Usually it will be necessary to add biocide as well as the ethoxylated phenol but sometimes the water will already contain sufficient biocide for this to be unnecessary.

Although it will normally be more convenient to add the ethoxylate and biocide as a mixture it is, of course, possible to add them to the water separately.

Typical ethoxylates which can be used in the present invention include those derived from phenol itself, nonyl phenol and dodecyl phenol. Typically, the number of ethoxylate groupings will vary from 4 to 15. In general, with increasing chain length of the alkyl phenol the number of ethoxylate groupings should also increase. A particular ethoxylate which has been found to give good results is that sold under the trade name Ethylan HB4. This is believed to be a phenol ethoxylate having about 4 ethoxylate units.

It has been found that the use of such ethoxylates is of general applicability and that beneficial results can be obtained with a variety of different types of biocide. The biocides usable in the present invention fall into one of the following classes:

(i) a substituted 5 or 6 membered ring heterocyclic compound in which the hetero atom or atoms are one or more of nitrogen, oxygen or sulphur and the substituent is an alkyl group, a keto group or a hydrosyl group or a halogen atom, such compounds include isothiazolones and in particular, those having the formula:



wherein R represents hydrogen or chlorine. A blend of these two isothiazolones is commercially available, the weight ratio of the chlorosubstituted compound to the unsubstituted compound being about 2.66:1. Dilute aqueous solutions of isothiazolones tend to be unstable on storage. To counteract this, inorganic salts in general, more particularly magnesium and copper salts, specifically copper nitrate, may be added;

(ii) a quaternary ammonium compound typically an N-alkyl, dimethyl benzyl ammonium chloride, specifically a product where the alkyl part is 50% C_{14}, 40% C_{12} and 10% C_{16};

(iii) a phenol or chlorinated phenol such as pentachlorophenol;

(iv) an amine or amide including 2,2-dibromo-3-nitrilopropionamide;

(v) a halogen release agent i.e. materials which liberate halogen (bromine, chlorine or iodine) when dissolved in water, including halogenated isocyanmates, halogenated hydantoins and alkyl derivatives of alkyl oxazolidinones, such as trichloroisocyanuric acid as well as chlorine itself and sodium and calcium hypochlorite;

(vi) an organic cyanide or thiocyanate, particularly methylene bis(thiocyanates);

(vii) a sulphone including halosulphones, particularly hexachlorodimethylsulphone;

(viii) a tin compound, particularly tributyltin oxide and chloride;

(ix) a straight chain aliphatic aldehyde, particularly glutaraldehyde;

(x) a triazine, particularly thio and/or amino-substituted alkyl triazines;

(xi) an alkyl phosphorium compound;

(xii) bis bromo acetoxy butene; and

(xiii) a dithiocarbamate, especially the monomethyl, dimethyl, monoethyl and diethyl derivatives, typically in the form of sodium salts.

It will, of course, be appreciated that some of these materials are not normally used by themselves but only in conjunction with other biocides.

A particular advantage of the use of the specified ethoxylates is that the ethoxylate can, in addition to improving the biocidal activity, act as a solvent for relatively insoluble biocides. This accordingly facilitates the introduction of the biocide to the system.

If the ethoxylate and biocide are added as a composition, the concentration of ethoxylate will, in general, be from 0.1 to 99.9% by weight. If the ethoxylate is to be used as a solvent it will generally be present at a concentration from 75 to 98% by weight. On the other hand, when the ethoxylate is not used as a solvent it will normally represent from 2 to 20%, especially 2 to 5% by weight of the composition. Clearly, if the ingredients are added to the water separately the same relative concentrations apply.

The amount of ethoxylate added to the system will normally be from 0.1 to 1000 ppm but, in general, it is sufficient to use 2 to 10 ppm and preferably 2 to 5 ppm. However, if the ethoxylate is being used as a solvent typical concentrations will be from 10 to 300 ppm. The concentrations of biocide will, of course, vary depending on the nature of the biocide and on the nature and amount of the bacteria present but, clearly, an amount effective to control the bacteria present should be used. As a rough guide, however, it can be said that the concentration of biocide (active ingredient basis) should vary from 0.5 to 250 ppm.

The biodispersant properties of the ethoxylate are such that, in some instances, it is possible to use a high concentration of the ethoxylate with a low concentration of biocide, especially to clean systems which have already become heavily bio-fouled as a result of past bacterial activity. Indeed, in some instances it is possible to dispense with the biocide altogether and merely disperse the fouled material with the aid of the ethoxylate and thus keep the heat exchange or other surfaces clean.

A preferred composition which can be used either for cooling water systems or paper making water systems has the formula by weight:

Water	82.25%
5-chloro-2-methyl-4-isothiazolin-3-one	1.36%
2-methyl-4-isothiazoline-3-one	0.51%
Magnesium Chloride	1.20%
Magnesium Nitrate	2.00%
Glutaraldehyde	7.50%
Copper Nitrate	0.18%
Ethylan HB4	5.00%

Other preferred compositions which can be used especially in cooling water systems include (i) a mixture of Ethylan HB4 (97% by weight) and methylene bis thiocyanate (3% by weight), (ii) a 10% aqueous solution of Ethylan HB4, (iii) an aqueous solution containing 5% by weight of Ethylan HB4 and 6.25% by weight of an N-alkyl, dimethyl benzyl ammonium chloride and (iv) a mixture of:

Ethylan HB 4	93.75%(by weight)
Methylene bis thiocyanate	1.00%
Hexachlorodimethylsulphone	4.00%
tributyl tin chloride	1.25%

In paper making, the ethoxylated phenol and, optionally, biocide may be added directly to the paper pulping bath or to the recirculating backwater, or indirectly, for example to a holding tank containing, generally moist, pulp or along with one or more chemical additives used in paper making. Such additives include starch, for example potato or corn starch, titanium dioxide, a defoamer such as a fatty acid alcohol, a size for example a rosin size based on abietic acid, a

neutral size based on alkyl ketene dimer or a succinic acid anhydride based size, a wet strength resin such as, if neutral, an epichlorohydrin polyamide or, if acid, a melamine- or urea-formaldehyde resin, various polymers used as dispersants or retention aids such as polyacrylates, polymethacrylates, polyamides and polyacrylamides, clay, chalk, fillers such as carboxymethyl cellulose, polyvinyl alcohol and optical brightening agents.

In cooling water systems, the ethoxylated phenol and, optionally, biocide may be introduced at any location where it will be quickly and efficiently mixed with the water of the system although it will generally be most convenient to add it to the make-up or feed water lines through which the water enters the system. Typically, an injector calibrated to deliver a predetermined amount periodically or continuously to the make-up water is employed. Of course, conventional water treatment additives such as dispersants, corrosion inhibitors, and lignin derivatives can also be included.

The following Examples further illustrate the present invention.

EXAMPLE 1

A mixture of water and slime from an industrial cooling tower was split into four parts. One part was used as a control, the second part was treated with 135 ppm of a mixture of isothiazolones (5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one in a ratio of 2.66:1), the third part was treated with 135 ppm of the mixture of isothiazolones and 600 ppm of aromatic ethoxylate (Ethylan HB4), and the fourth part was treated with 600 ppm of aromatic ethoxylate. Total bacterial counts were measured initially, and after 1 and 2 hours. Subsequently the second, third, and fourth parts of the mixture were re-treated as above, and total counts measured after 3 and 4 hours. Afterwards, the second, third and fourth parts of the mixture were again treated as above, and total counts measured after 5 and 6 hours. The results obtained are shown in the following Table.

TIME (HOURS)	TOTAL BACTERIAL COUNT/ML ON EACH PART OF THE SAMPLE			
	PART 1	PART 2	PART 3	PART 4
0	39.7×10^6	39.7×10^6	39.7×10^6	39.7×10^6
1	65.2×10^6	18.2×10^6	15.4×10^6	–
2	68.9×10^6	15.5×10^6	14.4×10^6	520×10^6
3	74.4×10^6	11.1×10^6	10.8×10^6	–
4	106.9×10^6	15.0×10^6	12.3×10^6	699×10^6
5	102.8×10^6	11.9×10^6	9.1×10^6	–
6	99.3×10^6	7.4×10^6	6.8×10^6	649×10^6

These results illustrate that the presence of the aromatic ethoxylate in combination with the biocide results in more effective microbiological control, as measured by reduced counts, than the presence of the biocide alone. In addition they show that the aromatic ethoxylate did not, on its own, have any biocidal action, but, in practice, led to increased counts, owing to its ability to disperse slime aggregates.

EXAMPLE 2

9 × 1 g samples of a microbiological slime from an industrial cooling system were each dispersed in 10 ml of water. One of these was used as a control and to the others were added the biocide and, in some cases, the aromatic ethoxylate used in Example 1, and the bacterial counts on each sample measured after 6 hours.

SAMPLE	MIXTURES OF ISOTHIAZOLONES	ADDITION AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	1.2×10^6
2	0.56 ppm	0	2.9×10^2
3	1.13 ppm	0	2×10^2
4	2.25 ppm	0	9
5	4.50 ppm	0	Nil
6	0.56 ppm	2.5 ppm	2.8×10^2
7	1.13 ppm	5.0 ppm	5
8	2.25 ppm	10.0 ppm	2
9	4.50 ppm	20.0 ppm	Nil

This Example shows increased effectiveness of the combination of the isothiazolones with the aromatic ethoxylate.

EXAMPLE 3

A mixture of water and slime from an industrial cooling system was split into 7 parts; each part was treated for two hours with the biocide and, in some cases, the aromatic ethoxylate, used in Example 1 as well as glutaraldehyde, and the total bacterial count on each part measured.

SAMPLE	ADDITION ISOTHIAZOLONES	GLUTARALDEHYDE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	0	1×10^6
2	0.9 ppm	3.7 ppm	0	1×10^3
3	1.8 ppm	7.4 ppm	0	3×10^2
4	3.7 ppm	14.8 ppm	0	6×10^1
5	0.9 ppm	3.7 ppm	2.5 ppm	2.5×10^2
6	1.8 ppm	7.4 ppm	5.0 ppm	8×10^1
7	3.7 ppm	14.8 ppm	10.0 ppm	7

This Example shows the presence of the aromatic ethoxylate increases the biocidal effectiveness of the isothiazolones and glutaraldehyde mixtures.

EXAMPLE 4

7 × 1 g samples of a microbiological slime from an industrial cooling system were each dispersed in 10 ml of water. One of these was used as a control and to the others were added the biocide and, in some cases, the aromatic ethoxylate, used in Example 1, as well as glutaraldehyde, and the total bacterial counts on each sample measured after 2 hours.

SAMPLE	ADDITION ISOTHIAZOLONES	GLUTARALDEHYDE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	0	1×10^6
2	0.9 ppm	3.7 ppm	0	8.5×10^2
3	1.8 ppm	7.4 ppm	0	6×10^2
4	3.7 ppm	14.8 ppm	0	1×10^2
5	0.9 ppm	3.7 ppm	2.5 ppm	4.5×10^2
6	1.8 ppm	7.4 ppm	5.0 ppm	1.5×10^2
7	3.7 ppm	14.8 ppm	10.0 ppm	8×10^1

This Example shows the increased effectiveness of the isothiazolones and glutaraldehyde mixtures in combination with the aromatic ethoxylate.

EXAMPLE 5

A mixture of water and slime from an industrial cooling system was split into three parts; the first part was used as a control and the other two parts treated for two hours with the following biocide and, in the third part, the aromatic ethoxylate used in Example 1 also, and the total bacterial counts measured.

SAMPLE	ADDITION		
	METHYLENE BISTHIOCYANATE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	23.9×10^6
2	5.7 ppm	0	17.9×10^6
3	5.7 ppm	10 ppm	11.9×10^6

The Example shows the increased effectiveness of the methylene bis thiocyanate-aromatic ethoxylate combination.

EXAMPLE 6

A mixture of water and slime from an industrial cooling system was split into three parts; the first part was used as a control and the other two treated for 2 hours with the following biocide and, in the third part, the aromatic ethoxylate used in Example 1 also, and the total count on each measured.

SAMPLE	ADDITION				
	METHYLENE BIS THIO-CYANATE	HEXACHLORO-DIMETHYL/ SULPHONE	TRIBUTYLTIN OXIDE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
0 (Control)	0	0	0	0	23.9×10^6
1	1.8 ppm	7.2 ppm	2.2 ppm	0	2.8×10^6
2	1.8 ppm	7.2 ppm	2.2 ppm	10	1.5×10^6

This Example shows the increased effectiveness of the methylene bis thiocyanate, hexachlorodimethyl sulphone, and tributyltin oxide mixtures when used with the aromatic ethoxylate.

EXAMPLE 7

3×1 g samples of a microbiological slime from an industrial cooling system were each dispersed in 10 ml of water. One of these was used as a control, and the other two treated for 6 hours with biocide and, with the third part, the aromatic ethoxylate used in Example 1 also, and the total counts on the samples measured.

SAMPLE	ADDITION		
	METHYLENE BIS THIOCYANATE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	$>1 \times 10^6$
2	3 ppm	0	1×10^6
3	3 ppm	97 ppm	7×10^3

This Example shows the increased effectiveness of the methylene bis thiocyanate-aromatic ethoxylate combination.

EXAMPLE 8

3×1 g samples of a microbiological slime from an industrial cooling system were each dispersed in 10 ml of water. One of these was used as a control, and the other two treated for 6 hours with biocide and, in the case of the third part, with aromatic ethoxylate as used in Example 1 also, and the total counts on the samples measured.

SAMPLE	ADDITION				
	METHYLENE BIS THIO-CYANATE	HEXACHLORO DIMETHYL SULPHONE	TRIBUTYL TIN OXIDE	AROMATIC ETHOXYLATE	TOTAL COUNT/ML
1 (Control)	0	0	0	0	1×10^6
2	1.0 ppm	4.0 ppm	1.2 ppm	0	1×10^6
3	1.0 ppm	4.0 ppm	1.2 ppm	93.8 ppm	3×10^3

This Example shows the increased effectiveness of the methylene bis thiocyanate, hexachlorodimethyl sulphone, and tributyl tin oxide mixture with aromatic ethoxylate.

EXAMPLE 9

Algae was allowed to develop and grow in tap water contained in a circular glass tank. The contents of the tank were stirred to give constant turbidity as measured by light transmission of a sample withdrawn from the tank. The aromatic ethoxylate used in Example 1 was introduced to give a concentration of 2 ppm. Within 20 minutes the turbidity of the dispersion as measured by light transmission had increased by 12.5%. For the next 15 minutes the turbidity remained constant, whereupon a further 3 ppm of the aromatic ethoxylate was added which led to a further 1.5% increase in turbidity.

This Example demonstrates the ability of the aromatic ethoxylate to disperse aggregates of algae.

EXAMPLE 10

Algae was allowed to develop and grow in tap water in a circular glass tank. The contents of the tank were stirred to give a constant turbidity as measured by light transmission of a sample withdrawn from the tank. 10 ppm of various different aromatic ethoxylates with the m and n values of the general formula given above was introduced into the tank, and the turbidity of the dispersion measured at various times by light transmission. The dispersants and penetrants studied, and the results obtained were:–

m	n	Transmission (%) Measured at Various Times			
		0	15 mins	30 mins	45 mins
6	9	100%	100 %	99.5%	97 %
9	9	100%	100 %	98 %	96.5%
10	9	100%	98.5%	98 %	95 %
15	9	100%	97.5%	97 %	95 %
30	9	100%	100 %	100 %	100 %
4	0	100%	100 %	92 %	89.5%
11	12	100%	98 %	93 %	85 %
10	12	100%	92 %	89.5 %	89.5 %

The results demonstrate the ability of the various ethoxylates listed to disperse algae. The only exception is the ethoxylated nonyl phenol containing 30 moles of ethylene oxide.

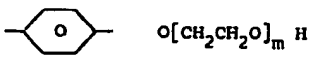
EXAMPLE 11

Two water samples taken from a paper machine system wwere divided into three parts. One part was used as a control the second part was treated with 13.5ppm of a mixture of isothiozolones (5-chloro-2-methyl-4-isothiazolin-3-one and 2-mehtyl-4-isothiazolin-3-one in the ratio 2.66:1) commercially available as Kathon WT, and the third part was treated with 13.5ppm of the mixture of isothiazolones and 10ppm or aromatic ethoxylate (Ethylan HB4). Total bacterial counts were measured initially and after 2 hours and 24 hours the results obtained are shown in the following table:–

Sample	Time (hours)	Total bacterial count/ml. on each part of the sample Part 1	Part 2	Part 3
1	0	1.8×10^5	1.8×10^5	1.8×10^5
	2	2.0×10^5	3.3×10^2	2.3×10^2
	24	2.7×10^5	3.9×10^4	8.3×10^3
2	0	2.3×10^5	2.3×10^5	2.3×10^5
	2	2.3×10^5	7.1×10^4	3.6×10^4
	24	2.3×10^6	2.8×10^4	1.9×10^4

CLAIMS

1. A method for the treatment of an aqueous system which comprises adding to the water either an ethoxylated phenol having the general formula:



where m represents 2 to 40 and R represents $C_n H_{2n+1}$ in which n is from 0 to 18 without a microbiological control agent or a said ethoxylated phenol and a microbiological control agent which is a biocide of one of the following formulae:

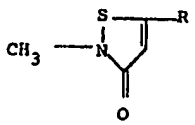
(i) a substituted 5 or 6 membered ring heterocyclic compound in which the hetero atom or atoms are one or more of nitrogen, oxygen or sulphur
(ii) a quaternary ammonium compound
(iii) a phenol or chlorinated phenol
(iv) an amine or amide
(v) a halogen release agent
(vi) an organic cyanide or thiocyanate
(vii) a sulphone
(viii) a tin compound
(ix) a straight chain aliphatic aldehyde
(x) a triazine
(xi) an alkyl phosphonium compound
(xii) bis bromo acetoxy butene; and
(xiii) a dithiocarbamate.

2. A method according to claim 1 wherein R represents hydrogen, or a nonyl or dodecyl radical.

3. A method according to claim 1 or 2 wherein m represents from 4 to 15.

4. A method according to any one of claims 1 to 3 wherein the ethoxylated phenol is a phenol ethoxylate having about 4 ethoxylate units.

5. A method according to any one of claims 1 to 4 wherein the biocide is an isothiazolone having the formula:



wherein R represents hydrogen or chlorine.

6. A method according to any one of claims 1 to 4 wherein the biocide is a quaternary ammonium compound, an amine, a phenol, a halogen release agent, a thiocyanate, a straight chain aliphatic aldehyde, a sulphone or a tin compound.

7. A method according to claim 6 wherein the biocide is an N-alkyl, dimethyl benzyl ammonium chloride, glutaraldehyde, methylene-bis thiocyanate, hexachlorodimethylsulphone or a tributyl tin oxide or chloride.

8. A method according to any one of the preceding claims which comprises adding to the water from 0.1 to 1,000 ppm of ethoxylate and from 0.5 to 250 ppm of biocide.

9. A method according to claim 8 which comprises adding to the water 2 to 10 ppm of the ethoxylate.

10. A method according to claim 9 which comprises adding to the water 2 to 5 ppm of

ethoxylate.

11. A method according to any one of the preceding claims for the treatment of an industrial cooling water system.

12. A method according to any one of claims 1 to 10 which comprises adding the ethoxylate and, optionally, biocide to a recirculating backwater used for the paper pulping bath used in paper making.

13. A method according to any one of claims 1 to 10 which comprises adding the ethoxylate and, optionally, biocide directly to the paper pulping bath used in paper making.

14. A method according to any one of claims 1 to 10 which comprises adding the ethoxylate and, optionally, biocide to a holding tank containing moist pulp used in paper making.

15. A method according to any one of claims 1 to 10 which comprises adding the ethoxylate and, optionally, biocide in combination with a chemical additive which is added to the paper pulping bath used in paper making.

16. A method according to claim 15 wherein the chemical additive is starch, titanium dioxide, a defoamer, a size, a wet strength resin, a dispersant or retention aid, a filler or an optical brightening agent.

17. A method according to claim 1 substantially as described in any one of the Examples.

18. A composition suitable for addition to an aqueous system which comprises a biocide as defined in any one of claims 1 and 5 to 7 and an ethoxylated phenol as defined in any one of claims 1 to 4.

19. A composition according to claim 18 which comprises from 0.1 to 99.9 per cent by weight of the ethoxylate.

20. A composition according to claim 18 which comprises 25 to 99 per cent by weight of the ethoxylate.

21. A composition according to claim 18 which comprises from 2 to 10 per cent by weight of the ethoxylate.

22. A compostion according to any one of claims 18 to 21 which also contains a chemical additive for a paper pulping bath.

23. A composition according to claim 22 wherein the chemical additive is starch, titanium dioxide, a defoamer, a size, a wet strength resin, a dispersant or retention aid, a filler or an optical brightening agent.

24. A composition according to any one of claims 18 to 21 which also contains paper pulp.

25. A composition according to claim 18 substantially as hereinbefore described.

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